

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/US04/043835

International filing date: 30 December 2004 (30.12.2004)

Document type: Certified copy of priority document

Document details: Country/Office: US
Number: 60/538,640
Filing date: 23 January 2004 (23.01.2004)

Date of receipt at the International Bureau: 09 February 2005 (09.02.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse

1277252

THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

January 24, 2005

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE.

APPLICATION NUMBER: 60/538,640

FILING DATE: *January 23, 2004*

RELATED PCT APPLICATION NUMBER: *PCT/US04/43835*



Certified by

Under Secretary of Commerce
for Intellectual Property
and Director of the United States
Patent and Trademark Office

16085
U.S. PTO
012304

Please type a plus sign (+) inside this box 

Approved for use through 04/30/2003. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

PROVISIONAL APPLICATION FOR PATENT COVER SHEET

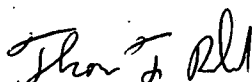
U.S. PTO
22264
60/538640

012304

INVENTOR(S)					
Given Name (first and middle [if any])		Family Name or Surname		Residence (City and either State or Foreign Country)	
David Alan Jeffrey Lee Ryan Christopher Thomas Dudley		RUSSO STRICKER SMITH CULP		AUDUBON, PENNSYLVANIA WYNNEWOOD, PENNSYLVANIA COLLEGEVILLE, PENNSYLVANIA DREXEL HILL, PENNSYLVANIA	
<input checked="" type="checkbox"/> Additional inventors are being named on the <u>1</u> separately numbered sheets attached hereto					
TITLE OF THE INVENTION (280 characters max)					
TRANSPARENT CONDUCTIVE OXIDE FILMS HAVING ENHANCED ELECTRON CONCENTRATION/MOBILITY, AND METHOD OF MAKING SAME					
Direct all correspondence to: CORRESPONDENCE ADDRESS					
<input type="checkbox"/> Customer Number		<input type="text"/>		<div>Place Customer Number Bar Code Label here</div>	
OR Type Customer Number here					
<input checked="" type="checkbox"/> Firm or Individual Name		Thomas F. Roland, Esq.			
Address		ATOFINA Chemicals, Inc.			
Address		2000 Market Street, 26th Floor			
City		Philadelphia	State	PA	ZIP 19103
Country		USA	Telephone	215-419-7314	Fax 215-419-7075
ENCLOSED APPLICATION PARTS (check all that apply)					
<input checked="" type="checkbox"/>	Specification	Number of Pages	16	<input type="checkbox"/>	CD(s), Number
<input type="checkbox"/>	Drawing(s)	Number of Sheets	<input type="text"/>	<input checked="" type="checkbox"/>	Other (specify)
<input type="checkbox"/>	Application Data Sheet. See 37 CFR 1.76				
					Claims-3 pages, Abstract-1 page
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT (check one)					
<input type="checkbox"/>	A check or money order is enclosed to cover the filing fees				FILING FEE AMOUNT (\$)
<input checked="" type="checkbox"/>	The Director is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number				01-2717
<input type="checkbox"/>	Payment by credit card. Form PTO-2038 is attached.				\$160.00
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.					
<input checked="" type="checkbox"/>	No.				
<input type="checkbox"/>	Yes, the name of the U.S. Government agency and the Government contract number are:				

Respectfully submitted,

SIGNATURE



TYPED or PRINTED NAME Thomas F. Roland, Esq.

TELEPHONE

215-419-7314

Date 01-23-04

REGISTRATION NO.

42,110

(if appropriate)

Docket Number:

IR 3723 PSP

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Mail Stop Provisional Application, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

P19LARGE/REV05

CERTIFICATE OF MAILING BY "EXPRESS MAIL" (37 CFR 1.10)

Applicant(s): RUSSO, D. et al

Docket No.

IR 3723 PSP

Serial No.

Not yet assigned

Filing Date

herewith

Examiner

Not yet assigned

Group Art Unit

Not yet assigned

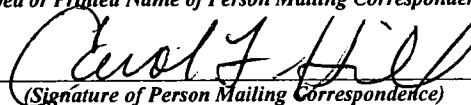
Invention: **TRANSPARENT CONDUCTIVE OXIDE FILMS HAVING ENHANCED ELECTRON CONCENTRATION/MOBILITY, AND METHOD OF MAKING SAME**

I hereby certify that the following correspondence:

Provisional Application for Patent Cover Sheet (in dup.); Certificate of Express mailing; and Provisional Application.

(Identify type of correspondence)

is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 in an envelope addressed to: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450 on

January 23, 2004*(Date)*Carol F. Hill*(Typed or Printed Name of Person Mailing Correspondence)**(Signature of Person Mailing Correspondence)*EV 269963534 US*("Express Mail" Mailing Label Number)***Note: Each paper must have its own certificate of mailing.**

Additional Page

Approved for use through 10/31/2002. OMB 0651-0032

U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Docket Number	IR 3723 PSP	Type a plus sign (+) inside this box →	+
---------------	-------------	-------------------------------------------	---

Number 2 of 2

WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

5 APPLICATION FOR
UNITED STATES LETTERS PATENT

10 of

15 David Alan RUSSO
Jeffrey Lee STRICKER
Ryan Christopher SMITH
Thomas Dudley CULP
Roman Yurevich KOROTKOV
and
20 Gary Stephen SILVERMAN

for

25 TRANSPARENT CONDUCTIVE OXIDE FILMS HAVING ENHANCED ELECTRON
CONCENTRATION/MOBILITY, AND METHOD OF MAKING SAME

30
35
40
45 Attorney Docket No.: IR 3723 PSP

5

10 TRANSPARENT CONDUCTIVE OXIDE FILMS HAVING ENHANCED ELECTRON
CONCENTRATION/MOBILITY, AND METHOD OF MAKING SAME

15 BACKGROUND OF THE INVENTION

Field of the Invention

20 This invention relates to transparent conductive oxide (TCO) films or coatings, and in particular to new multi- cation, thin film, n-type TCO films in which optimal electron concentration and mobility is achieved by selecting dopants having ionic sizes that approximate those of the oxide host material, and therefore are essentially non-disruptive to the host crystal lattice, thereby reducing electron scattering and increasing film conductivity.

25 The invention also relates to a method of forming TCO films or coatings by atmospheric pressure chemical vapor deposition (APCVD) of soluble solutions with a controlled crystallite size, quality and orientation to yield new n- type TCOs with enhanced electron concentration and mobility, and minimal defects.

30 The improved TCO films of the invention may be used in a variety of applications where performance of the films is affected by electron concentration and/or electron mobility, including solar control films in applications requiring a low plasma wavelength, and ohmic contact films in applications where low-resistivity is critical, such as in wide band gap semiconductor devices.

35

One of the applications of the TCO films or coatings of the invention is for use as solar control coatings, such as might be used on window glass. In general, it is desirable for such coatings to maximize transmittance of visible light while reflecting most infrared and near infrared (NIR) light. The amount of NIR light reflected depends on the “plasma wavelength,” which in a TCO coating or film is inversely proportional to the electron concentration in the coating. On the other hand, the transmittance of visible light by a TCO coating depends on electron mobility. In order to achieve an effective solar control coating, it is necessary to have a low plasma wavelength (or high plasma frequency), and high electron mobility. However, current thin film coating technologies permit only one of the two desired properties, electron concentration and electron mobility, to be optimized in a given film.

Much of the present research on thin film TCOs has focused on increasing conductivities, particularly with respect to Indium and/or Cadmium cation combinations. See, e.g., A.J. Freeman et al., MRS Bulletin, August 2000, pp. 45-51. However, even though In-Cd-O phases have some of the highest room temperature electrical conductivities measured for thin films (3500 S/cm), with mobilities as high as 200 cm²/Vs, electron concentrations were only 1x10²⁰ e/cm³, well below the typical 10²¹ for doped In₂O₃ films. On the other hand, some highly conductive In-Ga-Sn-O phases have conductivities as high as 3280 S/cm with measured electron concentrations of 8.6 x 10²⁰ e/cm³, but mobilities of only 24 cm²/Vs. Thus, in these prior art materials, either the electron concentration is too low to achieve an optimal plasma wavelength, or the electron mobility is too low to achieve optimal transmittance.

Most of the prior films were prepared using low pressure and plasma assisted chemical vapor deposition (CVD), and/or dc or rf sputtering techniques, as opposed to APCVD, as discussed above. Examples of currently used TCOs deposited by sputtering on glass include ZnO:Al, Cd₂SnO₄, Zn₂SnO₄, ZnSnO₃, ZrO₂, CeO₂, WO₃, and RuO₂. Examples of currently used TCOs may be deposited by conventional low pressure CVD include ZnO:In(Al, F, Ga), SnO₂:F, TiN, and In₂O₃:Sn (ITO). The best commercial thin film

TCO coating material, $\text{In}_2\text{O}_3:\text{Sn}$, has a plasma wavelength of 1 mm with an electron concentration of 10^{21} cm^{-3} .

One of the few approaches to increasing the conductivity of TCO films by using APCVD, as opposed to conventional low pressure CVD or sputtering, is described in U.S. Patent No. 6,524,647 (Varanasi et al.), which discloses APCVD of niobium doped tin oxide films. According to the Varanasi et al. patent, niobium is especially suited for replacing tin in the tin oxide lattice because it has a similar outer shell electron configuration and a comparable atomic number to that of tin. However, Varanasi et al. fails to optimize electrical properties because it fails to recognize that a key factor is actually the ionic size of the dopant, rather than atomic number or outer shell electron configuration.

In contrast, the present invention seeks to enable the ideal balance between electron concentrations, by selection of dopants according to the ionic size of the dopant relative to the oxide matrix, and appropriate control of the APCVD process used to deposit the doped oxides. None of the above-mentioned processes takes into account ionic size for the purpose of optimizing electron concentration and/or electron mobility.

SUMMARY OF THE INVENTION

It is accordingly a first objective of the invention to overcome the disadvantages of the prior art by providing TCO films having improved electrical properties, and that can be produced in an efficient and cost-effective manner.

It is a second objective of the invention to provide TCOs having high visible transmission and improved NIR reflective properties.

It is a third objective of the invention to provide transparent conductive oxides having high conductivity and an optimal combination of electron concentration and electron mobility for a given application.

It is a fourth objective of the invention to provide a method of making transparent conductive oxides that permits optimization of electron concentration and electron mobility, in order to improve visible transmission and NIR reflective properties, and/or to provide films having low resistivity and high work function.

It is a fifth objective of the invention to provide a method of using APCVD to deposit TCO films or coatings having improved electrical or optical properties.

These objectives of the invention are accomplished, in accordance with the principles of a preferred embodiment of the invention, by a variety of new n-type TCO films in which the dopants have ionic sizes that approximate those of the metal oxide host material, and that therefore are essentially non-disruptive to the host crystal lattice, reducing electron scattering and increasing film conductivity.

These objectives are further achieved by using atmospheric pressure chemical vapor deposition to deposit soluble solutions having ionic sizes that approximate those of the metal oxide host material to be deposited. The resulting doped metal oxide films have higher conductivities, which in turn imparts better NIR reflective properties to the films than, for example, the current state of the art tin doped indium oxide.

According to a first preferred embodiment of the invention, a metal oxide host, is deposited on a substrate in conventional fashion, but the dopants are chosen to approximately match the ionic size of the host crystals. Suitable hosts, with ionic size given in parentheses, include $\text{Zn}^{2+}(0.74\text{\AA})\text{O}$, $\text{Sn}^{4+}(0.71\text{\AA})\text{O}_2$, $\text{Ge}^{4+}(0.53\text{\AA})\text{O}_2$, $\text{Zr}^{4+}(0.80\text{\AA})\text{O}_2$, $\text{Ti}^{4+}(0.68\text{\AA})\text{O}_2$, or $\text{Ga}^{3+}(0.62\text{\AA})_2\text{O}_3$, while suitable dopants according to the invention include ions such as $\text{Sn}^{4+}(0.71)$, $\text{Bi}^{5+}(0.74\text{\AA})$, $\text{Ta}^{5+}(0.73\text{\AA})$, $\text{Hf}^{4+}(0.80\text{\AA})$, $\text{Mo}^{6+}(0.62\text{\AA})$, $\text{Te}^{6+}(0.59\text{\AA})$, $\text{Nb}^{5+}(0.70\text{\AA})$ and the like, all of which have sizes that approximate those of the metal oxide host material. The enhanced conductivity is manifest by both an increase of electron concentration and mobility as measured by the Hall effect.

According to a second preferred embodiment of the invention, a rutile MO_2 layer is deposited on SnO_2 or other metal oxide capable of stabilizing the rutile MO_2 film and optimize near infrared (NIR) reflection in glass/ SnO_2 / MO_2 bilayers and glass/ SnO_2 / MO_2 / SnO_2 sandwich structures. Suitable rutile MO_2 materials include but are not limited to $\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Mo}, \text{Ru}$, or mixed alloys thereof.

According to a third preferred embodiment of the invention, $\text{Sn}_x\text{M}_{1-x}\text{O}_2$ films are deposited on a substrate, where the metal- semiconductor transition of MO_2 films is modified by alloying with SnO_2 , thus optimizing the NIR reflection.

According to a fourth preferred embodiment of the invention, films such as but not limited to WO_3 , Mo_xO_y , A_xWO_3 , and $\text{A}_x\text{Mo}_{1-x}\text{O}_y$ are deposited on a substrate where A is H, Li, Na, and K, and $x = 0-2$ and high enough to modify the plasma wavelength to optimize the NIR reflectance. The film properties may be enhanced by APCVD deposition of WO_3 or Mo_xO_y on soda lime glass substrates with consecutive annealing/diffusion of Na, Li and K from the glass, and/or vapor phase incorporation/implantation of A into WO_3 .

Electron concentrations ranging from $7-10 \times 10^{20} \text{ e/cm}^3$ are possible with the novel n-type TCO films deposited by the above-described processes, as well as electron mobilities of $50-150 \text{ cm}^2/\text{vsec}$. In addition, these doped metal oxide films can be undercoated with one or more functional layers that can act as barrier layers to ion migration from the glass, anti-iridescent layers to reduce reflected color, and/or nucleation layers to alter the orientation of the TCO layer(s).

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a table illustrating the properties of MO_2 compounds with rutile structure manufactured according to the principles of the first preferred embodiment of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

As will be apparent from the examples set forth below, this invention provides a variety of new n-type TCO films, each having an ideal balance between electron concentration and mobility, by selecting dopants that are essentially non-disruptive to the host crystal lattice, thereby reducing electron scattering and increasing film conductivity. According to the method of the invention, the films are deposited on heated substrates such as glass by APCVD of organometallic precursors combined with specific dopants and other additives such that the deposited films have a higher electron concentration. The higher electron concentration is due to the incorporation of dopant ions in the host oxide lattice that cause little or no disruption of the lattice parameters, thereby decreasing electron scattering and increasing conductivity.

In a first preferred embodiment of the invention, doped metal oxide films are prepared by APCVD on a suitable substrate, such as soda lime glass, the metal oxides having crystal lattice host sizes ranging from .60Å to .80Å. Therefore, according to the principles of the invention, the ionic sizes of the dopants are also chosen to be approximately within this range. For example, suitable metal oxide hosts include, but are not limited to, $\text{Zn}^{2+}(\text{0.74}\text{\AA})\text{O}$, $\text{Sn}^{4+}(\text{0.71}\text{\AA})\text{O}_2$, $\text{Ge}^{4+}(\text{0.53}\text{\AA})\text{O}_2$, $\text{Zr}^{4+}(\text{0.80}\text{\AA})\text{O}_2$, $\text{Ti}^{4+}(\text{0.68}\text{\AA})\text{O}_2$, and $\text{Ga}^{3+}(\text{0.62}\text{\AA})_2\text{O}_3$, the ionic sizes of which are set forth in the parentheses. Ideal dopants for these metal oxide hosts include ions such as $\text{Sn}^{4+}(\text{0.71})$, $\text{Bi}^{5+}(\text{0.74}\text{\AA})$, $\text{Ta}^{5+}(\text{0.73}\text{\AA})$, $\text{Hf}^{4+}(\text{0.80}\text{\AA})$, $\text{Mo}^{6+}(\text{0.62}\text{\AA})$, $\text{Te}^{6+}(\text{0.56}\text{\AA})$, $\text{Nb}^{5+}(\text{0.70}\text{\AA})$ and the like, as well as combinations of any of the above-dopants.

In a second preferred embodiment of the invention, the principles of the invention are applied to hetero-epitaxial growth of APCVD-deposited doped and undoped rutile MO_2 structures, where $\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Mo}, \text{Ru}$ or mixed alloys thereof, on a SnO_2 or other metal oxide layer suitable for stabilizing the rutile MO_2 film and optimizing the near infrared reflection (NIR) in glass/ SnO_2 / MO_2 bilayers and glass/ SnO_2 / MO_2 / SnO_2 sandwich structures. Some of the MO_2 materials, such as CrO_2 , MoO_2 , RuO_2 , have

metallic conduction with high visible absorption. Others, such as TiO_2 , are semiconductors with band gaps of 3.0 eV and high visible transparency. Still others, such as VO_2 , have metal to semiconductor transitions at 340K. In all cases, however, the invention permits modification of the NIR reflectance of the coatings by depositing glass/ SnO_2 / MO_2 bilayers and glass/ SnO_2 / MO_2 / SnO_2 sandwich structures, where other metal oxides capable of stabilizing the rutile MO_2 layer may be substituted for SnO_2 . Since the host materials crystallize in a rutile structure, as illustrated in Fig. 1, it is expected that the deposited MO_2 films will crystallize in a similar fashion to produce epitaxial like layers. Also, since lattice parameters are close to that of SnO_2 for most of these materials, only small stresses are expected in (001) planes.

The third preferred embodiment of the invention involves a variation of the second preferred embodiment in which APCVD is used to grow $\text{Sn}_x\text{M}_{1-x}\text{O}_2$ ternary alloy system layers that modify the band gap parameters of SnO_2 . By tuning the fraction of the transition metal, one can obtain the necessary high NIR reflection with high electron concentration.

Finally, in accordance with the principles of a fourth preferred embodiment of the invention, APCVD is used to grow oxide coatings having the form WO_3 (as well as oxides such as Mo_xO_y) and A_xWO_3 , ($\text{A}_x\text{Mo}_{1-x}\text{O}_y$), where A is H, Li, Na, and K, and $x = 0-2$ and high enough to modify the plasma wavelength to optimize the NIR reflectance. In one embodiment, enhanced film properties are achieved by APCVD deposition of WO_3 or Mo_xO_y films on soda lime glass substrates with consecutive annealing/diffusion of Na, Li and K from the glass, and/or vapor phase incorporation/implantation of A into WO_3 .

Theoretical studies of A_xWO_3 indicate the possibility of a reflectance band shift towards the visible by increasing the fraction x of alkali metals in the ternary compound.

According to a preferred embodiment of the invention, the plasma wavelength of these coatings is tuned to 0.7 μm by varying the content of alkali metals in the coatings on glass and other substrates. Note that the amount of A is significantly higher than that

used in Li-doped WO_3 films prepared for their electrochromic properties, where alkali doping is typically less than a few percent. In addition, one can use Na (Li, K) diffusion from glass substrates in APCVD grown MO_x films to help promote formation of A_xMO_3 . In addition, implantation or vapor deposition of films with A may be used in this embodiment.

A predictive example of the first preferred embodiment of the invention, in which the doped metal oxide is tantalum doped zinc oxide, follows:

10 Predictive Example

A 2.2 mm thick glass substrate (soda lime silica), two inches square, is heated on a hot block to about 650°C . The substrate may be positioned about 25 mm under the center section of a vertical concentric tube coating nozzle. A carrier gas of dry oxygen flowing at a rate of 12.5 liters per minute (lpm) is then heated to about 1600°C and passed through a hot wall vertical vaporizer.

A liquid coating solution containing monobutyltin trichloride (MBTC) is fed to the vaporizer via a syringe pump at a volume flow designed to give a 0.5 mol % concentration in the gas composition. A second liquid coating solution of tetraethyl orthosilicate (TEOS) and triethyl phosphite (TEP) in a 1:1 mol ratio is fed to the vaporizer via a syringe pump at a volume flow designed to give a 0.5 mol % concentration in the gas composition.

The gas mixture is then allowed to impinge on the glass substrate for about 4 seconds to deposit a mixed oxide of tin and silicon about 80 nm thick with a refractive index of about 1.70. Immediately following, a second gas mixture composed of a diethylzinc tetraethylethylenediamine complex (DEED), a nitrogen carrier gas, tantalum (V) ethoxide, water vapor and air is caused to impinge on the metal oxide coated surface for about 30 seconds, resulting in a tantalum doped zinc oxide film of about 300 nm. The second gas mixture may be formed by mixing separate gas streams in a manifold just

before the coating nozzle. The water vapor and air are introduced at the top of the nozzle to minimize premature reaction with the zinc and tantalum precursors. The DEED liquid is fed via a syringe pump to a second vaporizer through which a nitrogen carrier gas is flowing at 160°C at about 10 lpm. The volume flow is preferably designed to give a 0.5 mol % concentration in the carrier gas.

Finally, the tantalum precursor is fed via a syringe pump to a third vaporizer through which a nitrogen carrier gas is flowing at 180 °C at about 10 lpm. The volume flow is designed to give a 0.1 mol % concentration in the carrier gas. Water is fed via syringe pump into a vaporizer through which an air carrier gas was flowing at about 10 lpm. The vapor concentration is about 3 mols per mol of zinc precursor.

The bilayer film stack made by the above method is predicted to have essentially no reflected color, a visible transmission greater than 70 %, an electron concentration in the range of $7\text{-}10 \times 10^{20} \text{ e/cm}^3$ and a mobility above $50 \text{ cm}^2/\text{v-sec}$ as measured by the Hall effect.

In a similar manner, hafnium doped zirconium dioxide, molybdenum doped gallium oxide and bismuth/tantalum doped tin oxide films could be prepared. In some cases, the precursors would be placed in heated bubblers and the carrier gas would pass through a molten liquid. These examples are only illustrative of the current invention and one skilled in the art will realize that minor variations outside these embodiments do not depart from the spirit and scope of this invention.

Having thus described various preferred embodiments of the invention in sufficient detail to enable those skilled in the art to make and use the invention, it will nevertheless be appreciated that numerous variations and modifications of the illustrated embodiment may be made without departing from the spirit of the invention. For example, other dopant and host combinations not mentioned herein could be used. Binary and tertiary dopant combinations could be found which might yield films with even higher conductivities. Other undercoat films could be used which have better barrier, anti-

reflection or nucleating layer properties than the combinations described herein. Anti-reflection layers could be placed on top of the doped metal oxide layer. Dopants could be incorporated into the host oxide layer in a gradient fashion; one dopant gradually decreasing while the other gradually increases in a continuum or step fashion. Separate
5 dopant layers could be combined. The dopants described herein all are intended to replace some of the metal host ions. The enhanced effect might also be accomplished by combining dopants of this invention with dopants such as fluorine that substitute for some of the oxygen atoms in the host matrix.

- 10 As a result, it is intended that the invention not be limited by the above description, but that it be defined solely in accordance with the appended claims.

What is claimed is:

1. A transparent conductive oxide (TCO) film comprising a doped metal oxide,
5 wherein the ionic size of at least one dopant in the doped metal oxide approximates the size of the host ions in an oxide lattice in the doped metal oxide.
2. The TCO film as claimed in claim 1, wherein the ionic size of said dopant is between approximately 0.6Å and 0.8Å.
- 10 3. The TCO film as claimed in claim 2, wherein said metal oxide is selected from the group consisting of Zn^{2+}O , Sn^{4+}O_2 , Ge^{4+}O_2 , Zr^{4+}O_2 , Ti^{4+}O_2 , $\text{Ga}^{3+}_2\text{O}_3$, and mixtures thereof, and wherein said at least one dopant is selected from the group consisting of Sn^{4+} , Bi^{5+} , Ta^{5+} , Hf^{4+} , Mo^{6+} , Te^{6+} , Nb^{5+} , and mixtures thereof.
- 15 4. A coated substrate comprising a substrate having directly coated thereon the TCO of claim 1.
5. A transparent conductive oxide (TCO) film comprising a rutile metal oxide MO_2 ,
20 wherein M is selected from the group consisting of Ti, V, Cr, Mo, Ru, and mixtures thereof.
6. The TCO film as claimed in claim 5, further comprising at least one M^1O_2 film layer, wherein said M^1O_2 film layer comprises SnO_2 or other metal oxide capable
25 of stabilizing the rutile MO_2 film.
7. The TCO film as claimed in claim 6, comprising a sandwich structure of $\text{M}^1\text{O}_2/\text{MO}_2/\text{M}^1\text{O}_2$.
- 30 8. The TCO film as claimed in claim 5, wherein said metal oxide is $\text{Sn}_x\text{M}_{1-x}\text{O}_2$, where M is selected from the group consisting of Ti, V, Cr, Mo, and Ru.

9. A coated substrate comprising a substrate having directly coated thereon the TCO of claim 5.
- 5 10. A transparent conductive oxide (TCO) film comprising a metal oxide A_xMO_y , wherein A is selected from the group consisting of H, Li, Na, and K, $x = 0-2$, and M is either W or Mo.
- 10 11. A coated substrate comprising a soda lime glass substrate and the TCO film as claimed in claim 10, wherein the metal oxide is deposited on the soda lime glass substrate with consecutive annealing/diffusion of Na, Li and K from the glass, and/or vapor phase with incorporation/implantation of A into A_xMO_y .
- 15 12. A method of depositing a metal oxide film by atmospheric pressure chemical vapor deposition (APCVD) on a substrate, comprising the step of exposing the heated substrate to a vapor including at least one dopant having an ionic size that approximates a size of host ions in an oxide lattice in the metal oxide.
- 20 13. The method as claimed in claim 12, wherein the ionic size of said dopant is between approximately 0.60\AA and 0.80\AA .
- 25 14. The method as claimed in claim 12, wherein said metal oxide is selected from the group consisting of $Zn^{2+}O$, $Sn^{4+}O_2$, $Ge^{4+}O_2$, $Zr^{4+}O_2$, $Ti^{4+}O_2$, $Ga^{3+}_2O_3$, and mixtures thereof, and wherein said at least one dopant is selected from the group consisting of Sn^{4+} , Bi^{5+} , Ta^{5+} , Hf^{4+} , Mo^{6+} , Te^{6+} , Nb^{5+} and mixtures thereof.
- 30 15. A method of depositing a metal oxide film by atmospheric pressure chemical vapor deposition (APCVD) on a substrate, comprising the step of exposing the heated substrate to a vapor containing chemical precursors to deposit at least one metal oxide wherein said metal oxide is rutile MO_2 , and M is selected from the group consisting of Ti, V, Cr, Mo, Ru and mixtures thereof.

16. The method of claim 15 wherein multiple metal oxide films are deposited by APCVD, wherein said multiple films comprise M^1O_2/MO_2 bilayers or $M^1O_2/MO_2/M^1O_2$ sandwich structures, wherein said M^1O_2 film layer comprises SnO_2 or other metal oxide capable of stabilizing the rutile MO_2 film.
17. The method of claim 15 wherein said metal oxide is $Sn_xM_{1-x}O_2$, where M is selected from the group consisting of Ti, V, Cr, Mo, and Ru.
18. A method of depositing metal oxide films by atmospheric pressure chemical vapor deposition (APCVD) on a substrate, comprising the step of exposing the heated substrate to a vapor containing chemical precursors to deposit at least one metal oxide, wherein said metal oxide is A_xMO_y wherein A is selected from the group consisting of H, Li, Na, and K, $x = 0-2$, and M is either W or Mo.

Fig. 1. MO₂ compound properties with rutile structure

MO ₂	a, Å	c, Å	V~10 ⁻²³ cm ⁻³	N _{Site} (Sn) ~10 ²² , cm ⁻³	N _{Site} (O) ~10 ²² , cm ⁻³	% dopant (O)*	E _G , eV	Thermal Expansion	Plasma ~ _p , ~m
SnO ₂	4.738	3.187	7.115	2.8	5.6	3.57	3.8	0.02	1.3 (7~10 ²⁰ cm ⁻³)
TiO ₂	4.585	2.95	6.2	3.22	6.45	3.1	3.0	0.114	
MnO ₂	4.396	2.871	5.548	3.6	7.2	2.7	Metal	0.05	

5

* - the required incorporation of a singly charged donor F, Cl, Br on O lattice site to obtain n = 2 ~10²¹ , cm⁻³ with the plasma wavelength of 0.77 ~m.

ABSTRACT OF THE DISCLOSURE

A variety of new n-type TCO films including films with dopants having ionic sizes that approximate those of the metal oxide host material, films with stabilized rutile
5 MO₂, and films with A_xMO_y. The films are deposited by APCVD.